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In this paper, some results obtained from the examination of some problems on the semi-commercial scale purification of rice oil, employing the method, above mentioned, are described. The main parts of the results are as follows.

1. If aqueous solution of sulphuric acid is used as one of the most effective washing agents against crude oil, the condition under which the decoloration effect and the yield of clear top oil are maximun, is that the concentration of the solution is about 10 % (wt.) and the rate of the solution added to the oil is about 18 % (vol.).

2. Concerning the mode of the emulsive washing, the agitation by air bubbles is more effective than that by a stirrer.

4. As one of the means in order to prevent the coloration of declored rice oil, caused by contacting the oil with iron material, the "passive" treatment of the iron surface is somewhat effective for oil whose acid value is lower than fifty.

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25. Studies on the Softening and Swelling Properties of Coal in Carbonization Process

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For the testing methods of the plastic state of coal, there are Shefield Laboratory Test, K. B. S.-method and Tadokoro's method etc.

Authors modified the K. B. S.-apparatus to obtain softening-swelling curve and gas evolution curve simultaneously. The used samples were of various ranks of coals (fuel ratio 0.5–5.0) in Japan.

By obtained softening-swelling curves, all samples were classified in three types, non-sottening type, softening type and softening-swelling type. Lignite or low rank coal and anthracite belonged to non-softening type, and were not caking. Bituminous coal belonged to the second or third type, and the fuel ratio range of softening type coals was between 1 and 3, and that of softening-swelling type coals was between 0.5 and 2.5

The critical points of these curves, softening temperature, maximum swelling temperature and temperature of maximum gas evolution rate, etc., were closely referred to the fuel ratio of coal samples.

The effects of size of coal and load to coal charge were examined with typical samples of each type, but no distinct conclusion was obtained. About artificial coals (prepared from cellulose, lignin, protein and their mixture in the medium of H_2O or N/10 NaOH) were also examined, but it was difficult to compare artificial coals with natural coals by softening swelling curve, owing to the difference of physical conditions.

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26. Studies on the Mechanism of Friedel-Crafts Type Reactions. (VIII)

Alkylation of Benzene by Organic Esters

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Esters of carboxylic acids can alkylate benzene in the presence of more than 1 mol aluminium halide per mol esters at the temperature below 50°C without accompanying acylation. (Bowden: J. Am. Chem. Soc. **60** 645 (1938)) Norris (J. Am. Chem. Soc. **62** 874 (1940)) obtained ethyl chloride and $CH_3COOAlCl_2$ when equimolecular amount of ethyl acetate and $AlCl_3$ was heated at 140–170°C and suggested the mechahism that the alkylation by the ester proceeds through an intermediate formation of alkyl halide (RCl). According to this mechanism the rate of formation of RCl and that of alkylation by the ester must be in the same order of magnitude, because the rate of alkylation of benzene by RCl is very large.

The authors studied the reactions between ethylacetate and $AlBr_3$ at 20°C (at this temperature ethylation of benzene proceeds smoothly). Only 4–9 % of ethylacetate was decomposed even in the presence of excess $AlBr_3$ without any formation of ethyl bromide. Kinetical studies showed that the rate of alkylation is first order in esters and its rate constant is proportional to the concentration of free $AlBr_3$ (i. e. total $AlBr_3$ concentration minus ester concentration). These result may be explained by the following mechanism: (1) only free $AlBr_3$ has catalytic activity and the $AlBr_3$ combined with the ester (1:1 mol complex) is catalyticaly inactive, (2) probably alkyl cation, accepted active intermediate of Friedel–Crafts reactions, may be formed by the interaction of free $AlBr_3$ and ester–$AlBr_3$ complex, (3) the alkyl cation alkylates benzene and never produces alkyl halide.

The velocity of alkylation is affected by structural change of R in the esters (R′COOR) in the order: ethyl acetate 0.41 $<$n–propyl acetate 0.82 $<$n–butyl acetate 0.85 (min^{-1} per mol/l $AlBr_3$). This order of reaction rate agrees with that of RCl and indicates that the inductive effect of alkyl group facilitate the attack of $AlBr_3$ on the oxygen atom of alkoxy group. The order of reaction rate caused by the structural change of R′ is as follows: ethyl formate 2.07 $>$ethyl acetate 0.41$>$ ethyl butyrate 0.084, which shows that the strengh of O–R bond is increased by the inductive effect of alkyl group in the acid residue.
